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Nonlinear elasticity and friction of liquid-crystalline polymer monolayers

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In the present paper we consider nonlinear elasticity and friction of grafted persistent chains, which are highly stretched in the normal to the surface direction due to orientational interactions. We examine the normal and the lateral forces both in equilibrium and under shear sliding when the monolayer is confined by a bare surface. We show that in the confined monolayer in equilibrium the tilted orientation of the director becomes stable. In the sliding regime the friction force passes through a maximum value. The additional normal force in the sliding regime, when the distance between the surfaces is fixed, is also considered. We show that this force is attractive for small velocities and becomes repulsive for high velocities after the friction force passes through the maximum value. © 1998 American Institute of Physics. [S0021-9606(98)50526-0]

I. INTRODUCTION

Thin surface monolayers formed by self-assembled molecules are very important both for technological applications and from a fundamental point of view for understanding of their elastic and frictional properties and those of more complicated supermolecular systems. Considerable progress has been made in the field of polymer brushes formed by long flexible chains grafted on a flat surface.^{1–3} The conformation of the chains in the brush becomes very stretched in the direction normal to the surface when the surface density of grafted points is high enough. However, such model system can not be effectively used for a description of monolayers formed by rather short self-assembled molecules. These monolayers very often have a liquid-crystalline (LC) or a crystalline ordering. Brushes with LC ordering have been investigated far less than isotropic brushes.^{4–8}

Recent experiments using Scanning Force Microscopy (SFM) and Surface Force Apparatus (SFA) technique revealed a strong correlation between the monolayer structure and their tribology.^{9–13} In particular, the friction force strongly depends not only on the interactions in the monolayer, which in most cases depends on the chemical nature of the chains, but also on the chain length. It suggests that the friction is connected with the elasticity of the monolayers.

In order to examine this assumption we consider a monolayer composed of chains with a persistent mechanism of flexibility. It is well known that orientational interactions

result in strong stretching of the persistent chain along the direction of the orientational field (so called stiffening effect¹⁴). It implies that grafted persistent chains can be aligned just due to the orientational interaction. In this paper we consider elasticity and frictional properties of a monolayer of persistent chains assuming that the orientational interactions are dominant.

II. MODEL AND FREE ENERGY

Our consideration starts with the formulation of the model. We assume that the persistent chains are grafted on a flat surface with an average distance d between neighbor grafted ends. It implies that the surface density satisfies $\nu_0 \approx d^{-2}$. The chain has a contour length L and a Kuhn segment length l , $L \geq l$. We also assume that the diameter of the chain $D < d$. The orientational interaction between the chains are described by a Maier–Saupe type potential in the following way. Let us divide the chain into segments of length $\lambda < l$, the total number of segments in the chain is $N = L/\lambda$. If the angle between the orientation \mathbf{n}_i of segment number i , and directing vector \mathbf{e}_z of the normal to the surface (axis z) is θ_i (Fig. 1), the energy of this segment is given by¹⁵

$$U(\mathbf{n}_i) = k_B T \frac{\lambda A}{2} \theta_i^2. \quad (1)$$

Here, the parameter A characterizes the molecular mean field. Actually this parameter depends on the concentration of segments or the volume fraction of the polymer and on the order parameter of the chain, which should be calculated from a self-consistency condition.¹⁴ It implies that generally A depends on the coordinate z . However, for the stretched

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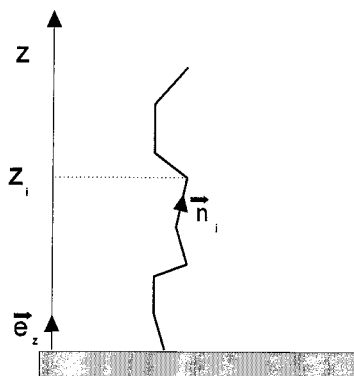


FIG. 1. Chain model.

persistent chains this dependence is important only in a small region near the grafting surface and near the free boundary of the layer, where fluctuations are large. In the other region of the layer the parameter A is practically independent of the coordinate z and we will employ this approximation throughout. We will also assume a linear dependence of the parameter A on the volume fraction of the polymer in the layer ϕ , $A \propto \phi$, where the volume fraction is connected with the height H of the monolayer by

$$\phi = (LD^2)/(Hd^2). \quad (2)$$

Obviously $\phi \leq 1$, therefore $H \geq H_{\min} = L(D/d)^2$. Thus the parameter A can be written in the form

$$A = A_0 \frac{L}{H}, \quad (3)$$

where $A_0 = \text{const}$. Equation (1) can be considered as the asymptotic limit of the Maier-Saupe potential when the orientation is high. Thus the total orientational energy of one chain is a sum $\sum_{i=1}^N U(\mathbf{n}_i)$, which in the continuum limit can be written as

$$U_{\text{tot}} = k_B T \frac{A}{2} \int_0^L \theta^2(s) ds. \quad (4)$$

Obviously, the orientation of two successive segments, \mathbf{n} , \mathbf{n}' , is not independent, but connected by the transition probability $g(\mathbf{n}|\mathbf{n}')$,¹⁶ which can be obtained from the expression for the elastic energy of the continuum model of the persistent chain^{17,18}

$$U_{el} = k_B T \frac{l}{4} \int_0^L \left(\frac{d\mathbf{n}}{ds} \right)^2 ds, \quad (5)$$

and is given by

$$g(\mathbf{n}|\mathbf{n}') \sim \exp\left(-\frac{l}{4\lambda} (\mathbf{n} - \mathbf{n}')^2\right). \quad (6)$$

Here $k_B T(l/4\lambda)(\mathbf{n} - \mathbf{n}')^2$ is the elastic bend energy.

Let us denote the z coordinate of segment i along the chain as z_i (Fig. 1). Then we can introduce the N -particle distribution function ρ as follows

$$\begin{aligned} \rho(\mathbf{n}_1, z_1 | \mathbf{n}_2, z_2 | \dots | \mathbf{n}_N, z_N) \\ = C \delta(z_1 - \lambda \cos \theta_1) g(\mathbf{n}_1 | \mathbf{n}_2) \\ \times \delta(z_2 - z_1 - \lambda \cos \theta_2) e^{-U(\mathbf{n}_2)} g(\mathbf{n}_2 | \mathbf{n}_3) \\ \times \delta(z_3 - z_2 - \lambda \cos \theta_3) e^{-U(\mathbf{n}_3)} \dots, \end{aligned} \quad (7)$$

where C is a normalization constant. The distribution function of the free end is given by

$$\begin{aligned} \psi(L, \mathbf{n}_1, \mathbf{n}, z) = \int dz_1 d\mathbf{n}_2 dz_2 \dots d\mathbf{n}_{N-1} dz_{N-1} \\ \times \rho(\mathbf{n}_1, z_1, \mathbf{n}_2, z_2, \dots, \mathbf{n}_{N-1}, z_{N-1}, \mathbf{n}, z). \end{aligned} \quad (8)$$

Note that the orientation of the grafted end, \mathbf{n}_1 , is fixed. The differential equation for this function can be derived by adding a new segment to the chain keeping the concentration and hence the parameter A constant. After transition to the continuum limit the equation is given by

$$\frac{\partial \psi}{\partial L} = \frac{1}{l} \Delta_{\mathbf{n}} \psi - \cos \theta \frac{\partial \psi}{\partial z} - \frac{A \theta^2}{2} \psi. \quad (9)$$

This equation coincides with the equation for the statistical sum of the chain, which is proportional to or equals ψ , depending on the normalization condition.¹⁹ Thus the problem reduces to the solution of the differential equation (9).

The equation can be solved analytically in the asymptotic case, when the chain is strongly stretched, so that $L - z \ll L$. Using the approximation $\cos \theta \approx 1 - \theta^2/2$, and assuming that the bend takes place in one plane, $\Delta_{\mathbf{n}} \psi = \partial^2 \psi / \partial \theta^2$, the solution has the form

$$\psi(L, \theta_1, \theta, z) \sim \sqrt{\frac{l}{L-z}} \exp\left(-\frac{U(L, \theta_1, \theta, z)}{k_B T}\right), \quad (10)$$

where

$$\begin{aligned} U(L, \theta_1, \theta, z)/k_B T \approx \frac{L^2}{8l(L-z)} + \frac{(\theta_1^2 + \theta^2)L}{8(L-z)} \\ + \frac{(\theta_1^2 + \theta^2)^2 l}{32(L-z)} + A(L-z). \end{aligned} \quad (11)$$

Here we kept the principal terms of the expansion. Note that A depends on the height of the layer H , Eq. (3). In the mean field approximation U is the free energy per chain. It contains two main contributions. The first contribution arises from the orientational interaction and is given by the last term in Eq. (11). The orientational energy is minimal when the chain is completely stretched ($z=L$). The parameter $k_B T \cdot A$ equals the molecular stretching force. The second contribution is connected with the chain elasticity and can be divided in two parts: the loss of entropy of the chain due to stretching [the first term in Eq. (11)] and the elastic bend energy (the second and the third term). The contribution from the chain elasticity is easy to understand if we write the first term of Eq. (11) as (L/x_c) where the length

$$x_c = \frac{8l(L-z)}{L} \quad (12)$$

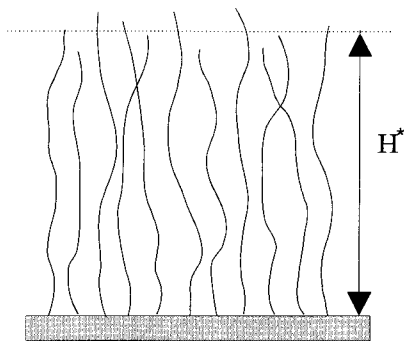


FIG. 2. Schematic illustration of the free monolayer.

can be identified with the correlation length of the chain. The second term of Eq. (11) follows from Eq. (5) for the elastic energy if we assume that the bending takes place on a section of length x_c near the chain ends, $\Delta U_{el} = (l/4) \int_0^L (d\theta/ds)^2 ds \approx (l/x_c)(\theta^2 + \theta_1^2)$, which gives the corresponding term. It justifies the definition of x_c as the correlation length. Note that the above equations are correct when $x_c < l$.

From now on we will assume that the grafted segments are oriented normally to the surface, $\mathbf{n}_1 = \mathbf{e}_z$ ($\theta_1 = 0$). Let us first estimate the equilibrium height H^* of the free monolayer (Fig. 2). This can be done in the following way. If $z^*(H)$ is the equilibrium position of the chain tail when H is fixed, then the equilibrium height can be estimated from the self-consistency condition $z^*(H^*) = H^*$. In order to calculate z^* we first average the free energy, Eq. (11), over the angles θ which are distributed according to the distribution function ψ , Eq. (10)

$$U^*(L, z) = \langle U(L, \theta, z) \rangle_\theta = k_B T \int \psi(L, \theta, z) \ln \psi(L, \theta, z) d\theta. \quad (13)$$

Integration gives the average free energy

$$U^*(L, z)/k_B T \approx U_0 + \frac{L^2}{8l(L-z)} + \frac{3l}{2L^2} (L-z) + \frac{A_0 L}{H} (L-z). \quad (14)$$

Here $U_0 = \text{const}$, and the third term is connected with the elastic energy. We will assume that orientational energy (the last term) exceeds the elastic energy. Therefore, there are only two main contributions to the free energy, namely the loss of the entropy due to the stretching and the orientational energy

$$\Delta U^*(L, z)/k_B T \approx \frac{L^2}{8l(L-z)} + \frac{A_0 L}{H} (L-z). \quad (15)$$

Minimization of this free energy with respect to z , using the self-consistency condition, results in the equilibrium height of the monolayer

$$H^* = L \left(1 - \frac{1}{2\sqrt{2A_0 l}} \right). \quad (16)$$

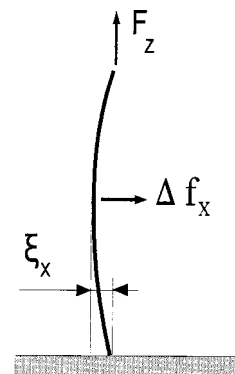


FIG. 3. Geometry of forces when the middle part of the chain displaces in the lateral direction.

Obviously the chain is strongly stretched, and our consideration is valid if $A_0 l \gg 1$. We will assume that this condition is fulfilled. After expansion of the free energy, Eq. (15), around equilibrium we find for the size of the fluctuations in the normal direction

$$\xi_z \sim \sqrt{Ll} \frac{1}{(A_0 l)^{3/4}}. \quad (17)$$

In order to estimate the size of the fluctuations in the lateral direction, we note that the chain is stretched by the force $F_z \sim A_0$. Therefore any deviation of the chain tail (or of the middle part of the chain, Fig. 3) on a distance $\sim \xi_x$ in the lateral direction implies (from the geometry of the forces) that a restoring force $\Delta f_x \sim F_z \varphi$ appears, where $\varphi \sim \xi_x/L$. The energy connected with this deviation is $\Delta U_x \sim \Delta f_x \xi_x$. The characteristic fluctuation size ξ_x , follows from the condition $\Delta U_x \sim k_B T$

$$\xi_x \sim \sqrt{Ll} \frac{1}{(A_0 l)^{1/2}}. \quad (18)$$

Note for $A_0 l \sim 1$, $\xi_x \sim \xi_z \sim \sqrt{Ll}$. Thus the conformation of the chain in the monolayer is nearly completely stretched with small fluctuations in the normal and lateral directions.

III. EFFECT OF EXTERNAL LOAD AND SHEAR DEFORMATION

In this section we consider the behavior of the monolayer confined between two flat surfaces, separated by a distance $H < L$. We start with the situation $H > H^*$. In this case the external force f_z is determined by fluctuations. In order to find the dependence of the force f_z on the distance H let us introduce a distribution function of the free end, $\psi(z)$. The free energy per chain is given by

$$F = \int_0^H dz (k_B T \psi(z) \ln \psi(z) + \psi(z) \Delta U^*(z)), \quad (19)$$

where $\Delta U^*(z)$ was defined in Eq. (15), and the molecular field $A = A_0 L/H^*$. Minimization with respect to ψ results in a Boltzman distribution for the function ψ , $\psi(z) = C \times \exp(-\Delta U^*(z))$, $C = \int_0^H \exp(-\Delta U^*(z)/k_B T) dz$ is the normalization constant. Further elimination of ψ from the Eq. (19) results in the free energy as a function of H

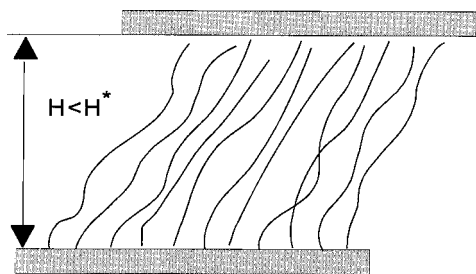


FIG. 4. Schematic illustration of the confined monolayer.

$$F = -k_B T \ln \int_0^H \exp(-\Delta U^*(z)/k_B T) dz. \quad (20)$$

The external normal force can be defined in the usual way, $f_z = \partial F / \partial H$, and equals

$$f_z = -k_B T \psi(H) \approx -\frac{1}{\xi_z} \exp\left(-\frac{L^2}{8l(L-H)}\right). \quad (21)$$

The sign of this force is negative, which implies a repulsion between the surfaces. As it follows from Eq. (21), the external force is balanced by the ideal-gas pressure of the free chain ends. For $H \sim H^*$ the force is still exponentially small.

In order to calculate the normal force for $H < H^*$ we have to take into account two things. First the molecular field A depends on the distance H , therefore minimization should be done using this fact. Second, the initial normal to the surfaces orientation of the layer could be unstable with respect to the tilt. Let us assume at first that the vector of the layer orientation is directed perpendicular to the surfaces. In this case the free energy (20) in a first approximation can be written as

$$F = \Delta U^*(H) = k_B T \left[\frac{L^2}{8l(L-H)} + \frac{A_0 L}{H} (L-H) \right]. \quad (22)$$

This approximation corresponds to the mean field. The external normal force is given by

$$f_z = k_B T \left[\frac{L^2}{8l(L-H)^2} - \frac{A_0 L^2}{H^2} \right]. \quad (23)$$

The sign of this force is negative for $H < H^*$ (the second term is dominant). We will not consider here the fluctuation corrections, which are important for $H \sim H^*$ and which bridge these two regimes. Actually the repulsion force is very small for $H \sim H^*$ and is not important for the next discussion.

Next we take into account the tilting of the monolayer (Fig. 4, $H < H^*$). The free energy of the monolayer having an orientation which is tilted with respect to the normal vector of the surface, can in the mean field approximation be derived from Eq. (22) by changing the system of coordinates. If the system of coordinates rotates over some angle, so that after the transformation the tail has coordinates (H, x) , the distance between the chain ends is given by $r = \sqrt{H^2 + x^2}$ [before the transformation the coordinates of the tail were $(r, 0)$]. Taking into account the fact that the bend elastic en-

ergy is small, and the molecular field parameter A depends only on the height H of the monolayer, the free energy per chain can be written as

$$F^*(H, x) = k_B T \left[\frac{L^2}{8l(L-r)} + \frac{A_0 L}{H} (L-r) \right]. \quad (24)$$

The external load f_z and external shear force f_x applied to the monolayer (per chain) can be expressed through the free energy F^* in the usual way:

$$f_z = \left(\frac{\partial F^*}{\partial z} \right)_{x=\text{const}}; \quad f_x = \left(\frac{\partial F^*}{\partial x} \right)_{z=\text{const}}. \quad (25)$$

The equilibrium tilt angle $\theta^* = \arctan(x^*/H)$ for a fixed H , which corresponds to the minimum of the free energy, follows from the equation $f_x(x^*) = 0$

$$\theta^* = \arctan \sqrt{\frac{L^2}{H^2} \left(1 - \sqrt{\frac{H}{2A_0 l}} \right) - 1}. \quad (26)$$

Note that the term under the square root is always positive for $H < H^*$, where our approach applies, and therefore the confined layer has always a tilted orientation. Any displacement of the chain tails in the lateral direction over a distance x_1 with respect to the equilibrium point x^* results in the lateral force

$$f_x = k_B T \frac{(2A_0 l)^{3/2}}{L l} \left(\frac{L}{H} \right)^{3/2} \left(1 - \frac{H^2}{L^2} \right) x_1. \quad (27)$$

Actually $x_1 < \Delta x_{\text{max}} = x_{\text{max}} - x^* \approx L \sqrt{LH/8A_0 l(L^2 - H^2)}$, where $x_{\text{max}} = \sqrt{L^2 - H^2}$ is the maximum lateral displacement.

Similarly we can calculate the normal force as a function of the distance H , when the tails of the chains are displaced over a distance $x^* + x_1$ in the lateral direction with respect to their grafted ends

$$f_z = k_B T \left[-\frac{1}{2l} \left(\frac{A_0 l}{2} \right)^{1/2} \left(\frac{L}{H} \right)^{3/2} + \frac{(2A_0 l)^{3/2}}{L l} \left(\frac{L}{H} \right)^{1/2} \sqrt{\left(1 - \frac{H^2}{L^2} \right) x_1} \right]. \quad (28)$$

The first term of this equation is dominant and is connected with increasing of the internal energy under compression, and the second term arises due to nonlinearity and implies the additional normal force which is connected with the lateral force by the rule of the force geometry

$$\Delta f_z = -f_x \tan^{-1} \theta^*. \quad (29)$$

Thus if we apply shear deformation to the loaded monolayer and try to keep the distance H constant, we should decrease the external load.

The fluctuations of the tail along the tilted axis and perpendicular to this axis can be found similarly to the unloaded layer and the corresponding quantities are given by Eqs. (17) and (18), where A_0 should be replaced by $A = A_0 L/H$.

IV. FRICTION BEHAVIOR

We apply the above results to the problem of friction between the flat monolayer and the flat bare surface, which

confines the monolayer. We will assume that the distance between the surfaces H is constant and will calculate the friction force and the additional normal force, which appears when a shear velocity u is imposed to one of the surfaces. In order to introduce friction we have to define a mechanism of dissipation, which we assume to be connected with the relaxation interaction between the tails of the chains and the bare surface. In order to describe this interaction we will follow our previous model²⁰ and introduce a thin adsorbed layer of thickness a on the free surface so that a free segment adsorbs and desorbs for a time τ . It is assumed that this time is the same for both processes so that the surface is neutral and our previous results can be applied to this situation. Note that a difference between adsorption and desorption times for the free segments implies an additional interaction in the system which should be taken into account when the equilibrium properties are considered.

Coming back to the definition of the relaxation time τ , we assume the activation mechanism of relaxation, which means that the time can be written in the form

$$\tau = \tau^* e^{V_a/k_B T}, \quad (30)$$

where V_a is an activation energy and τ^* is the characteristic oscillation time of a segment in a local potential well. The situation becomes different when instead of a free segment, a segment belonging to the chain tail is considered. In order that the tail desorbs from the surface it should overcome not only the activation barrier but also the potential barrier which is connected with the change of the free energy of the chain. This last one depends on the correlation between the thickness of the adsorbed layer, a , and the magnitude of the fluctuations of the tail, ξ . As mentioned before, the size of the fluctuations is different along the orientational axis and perpendicular to this axis, and they are anisotropic. In order to avoid this additional complication we will assume the isotropic approximation, and thus define the size of the fluctuations in the normal to the surface direction as $\xi \sim (Ll)^{1/2} (H/A_0 l)^{3/4}$ [see Eq. (17) with the renormalized parameter A_0]. The additional potential barrier, which the tail should overcome, is then approximately

$$\Delta V_a \approx k_B T \frac{a^2}{\xi^2} \approx \left(\frac{A_0 l L}{H} \right)^{3/2} \frac{a^2}{Ll}. \quad (31)$$

Thus the desorption time is given by

$$\tau_- = \tau^* e^{V_a + \Delta V_a/k_B T}. \quad (32)$$

When $a \leq \xi$, $\Delta V_a \sim k_B T$, and the additional barrier is not important.

The situation is opposite for the adsorption time. When the tail adsorbs, it wins the energy ΔV_a , therefore adsorption occurs more easily, and the characteristic adsorption time is

$$\tau_+ = \tau^* e^{V_a - \Delta V_a/k_B T}. \quad (33)$$

We will consider the general case, $\Delta V_a \gg k_B T$. When the surface slides with a velocity u with respect to the monolayer, the dynamics of the chain is as follows. If the velocity u is small, $u\tau_- < \Delta x_{\max}$ (we define it as regime 1), the adsorbed tail first moves along the x -axis and then breaks after a time τ_- , then the chain relaxes very fast to the minimum

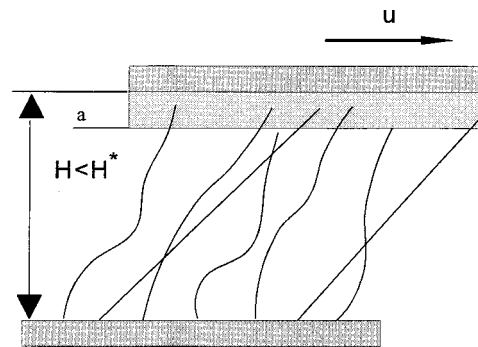


FIG. 5. The monolayer in the sliding regime.

of the energy, and after a time τ_+ adsorbs again. After that the circle is repeated. The lateral friction force (per unit area), which should be applied in order to keep the velocity constant, can be found from Eq. (27) when $x_1 = u\tau_-$

$$F_x \approx \nu_0 k_B T \frac{(2A_0 l)^{3/2}}{Ll} \left(\frac{L}{H} \right)^{3/2} \left(1 - \frac{H^2}{L^2} \right) u \tau_-. \quad (34)$$

Similarly we find the additional normal force from Eq. (28)

$$\Delta F_z \approx -\nu_0 k_B T \frac{(2A_0 l)^{3/2}}{Ll} \left(\frac{L}{H} \right)^{1/2} \sqrt{1 - \frac{H^2}{L^2}} \cdot u \tau_-. \quad (35)$$

This force is negative and hence implies an additional attraction between the surfaces.

After the imposed velocity exceeds the critical value

$$u_1 = \frac{\Delta x_{\max}}{\tau_-}. \quad (36)$$

the tails cannot break thermally any more and the breakage is connected with the limited extensibility of the chains (regime 2). The friction force has two contributions in this case, namely from the elongating chains and from the breaking chains (Fig. 5). The average force (per chain) in the elongation stage can be approximately obtained from Eq. (34) averaging on the interval $0 < u\tau_- < \Delta x_{\max}$

$$f_x^{el} \approx k_B T A_0 \frac{\sqrt{L^2 - H^2}}{H}. \quad (37)$$

The additional normal attractive force is

$$\Delta f_z^{el} \approx -k_B T A_0. \quad (38)$$

Let us consider the breakage stage. In this case both the lateral and the normal forces and the lateral velocity and the velocity of breakage can be found from geometric arguments. The breakage velocity is (the tangential of the angle between the orientational axis and the z -axis is $\tan \theta = \sqrt{L^2 - H^2}/H$)

$$u_z = u \tan^{-1} \theta = u \frac{H}{\sqrt{L^2 - H^2}}. \quad (39)$$

The breakage time is therefore $\tau_b \sim a/u_z$. In order to calculate the normal breakage force we use the following arguments. If the force Δf_z is applied to the adsorbed segment, the segment is desorbed after a time

$$\tau(\Delta f_z) \approx \tau^* e^{V_a + \Delta V_a + \Delta f_z a / k_B T}, \quad (40)$$

(the sign of this force is negative because it is directed against the direction of the z -axis). In our case the breakage time is τ_b , hence the breakage force follows from the equation $\tau_b \approx \tau(\Delta f_z^{br})$

$$\begin{aligned} \Delta f_z^{br} &\approx -\frac{k_B T}{a} \ln \frac{u_z \tau_-}{a} \\ &\approx -\left(\frac{V_a}{a} + \left(\frac{A_0 l L}{H}\right)^{3/2} \frac{a}{Ll} + \frac{k_B T}{a} \ln \frac{u \tau^*}{a}\right). \end{aligned} \quad (41)$$

From the geometry of the forces we find the lateral force

$$\begin{aligned} f_x^{br} &\approx -\Delta f_z^{br} \tan \theta \\ &\approx \frac{\sqrt{L^2 - H^2}}{H} \left(\frac{V_a}{a} + \left(\frac{A_0 l L}{H}\right)^{3/2} \frac{a}{Ll} + \frac{k_B T}{a} \ln \frac{u \tau^*}{a}\right). \end{aligned} \quad (42)$$

Note that the forces act only during the breakage time τ_b . The total life time of the chain in the adsorbed state is determined by the elongation time

$$t^* = \frac{\Delta x_{\max}}{u} \approx \frac{L}{u} \sqrt{\frac{LH}{8A_0 l (L^2 - H^2)}}. \quad (43)$$

Thus the friction force per unit area can be written as

$$F_x = \nu_0 \left(f_x^{el} + \frac{\tau_b}{t^*} f_x^{br}\right) \quad (44)$$

and the additional normal force, which is attractive, is given by

$$\Delta F_z = \nu_0 \left(\Delta f_z^{el} + \frac{\tau_b}{t^*} \Delta f_z^{br}\right). \quad (45)$$

So far we did not take into account the effect of the desorbed chains on the normal pressure. The fraction of these chains in regime 2 is $\tau_+ / (\tau_+ + t^*) \approx \tau_+ / t^*$ (here we assume that $\tau_+ < t^*$). The desorbed chains are compressed by a force of the order

$$f'_z \sim k_B T \frac{a}{\xi^2} \approx k_B T \left(\frac{A_0 l L}{H}\right)^{3/2} \frac{a}{Ll} \quad (46)$$

and their reaction is directed against the external pressure and thus positive. The origin of this force becomes clear by noting that the reaction of the adsorbed layer is elastic on a time scale smaller than τ_+ , and thus the desorbed chains press on the boundary of the adsorbed layer. The contribution from the desorbed chains to the additional normal force per unit area is

$$\Delta F'_z \approx \nu_0 f'_z \frac{\tau_+}{t^*} \quad (47)$$

and the total additional normal force is the sum $\Delta F_z^{\text{tot}} = \Delta F_z + \Delta F'_z$, where the sign of these forces is opposite. The attrac-

tion is dominant in this case. Finally the friction and the normal forces in regime 2 can approximately be written as

$$\begin{aligned} F_x &\approx \nu_0 k_B T \frac{\sqrt{L^2 - H^2}}{H} \\ &\times \left(A_0 + \frac{(8A_0 l)^{1/2}}{(LH)^{1/2}} \left(\frac{L^2 - H^2}{LH}\right) \ln \frac{u \tau_-}{a}\right), \end{aligned} \quad (48)$$

$$\begin{aligned} \Delta F_z &\approx -\nu_0 k_B T \left(A_0 + \frac{(8A_0 l)^{1/2}}{(LH)^{1/2}} \left(\frac{L^2 - H^2}{LH}\right) \ln \frac{u \tau_-}{a}\right) \\ &+ 2\sqrt{2} \nu_0 k_B T \left(\frac{A_0 l}{H}\right)^2 \frac{a \sqrt{L^2 - H^2}}{Ll} u \tau_+. \end{aligned} \quad (49)$$

The last regime (regime 3) corresponds to high velocities, when $\tau_+ < t^*$ or $u > u_2$, where

$$u_2 = \frac{\Delta x_{\max}}{\tau_+}. \quad (50)$$

The important feature of this regime is the decrease of the fraction of adsorbed chains. Indeed, the chains spend a time t^* in the adsorbed state, whereas in the desorbed state the time is τ_+ . Hence the fraction of adsorbed chains is proportional to $t^*/(\tau_+ + t^*)$. Taking into account the fact that the dynamics of the chains in this regime is the same as in regime 2, the main results can be obtained in a similar manner. The principle difference is in the statistics of the adsorbed and desorbed chains. Thus based on the above arguments, the friction force and the additional normal force can be derived from the corresponding equations [Eqs. (41), (42), (44)–(47)]:

$$F_x \approx \nu_0 \frac{t^*}{\tau_+} \left(f_x^{el} + \frac{\tau_b}{t^*} f_x^{br}\right), \quad (51)$$

$$\Delta F_z^{\text{tot}} \approx \Delta F_z \frac{t^*}{\tau_+} + \Delta F'_z. \quad (52)$$

After some calculations the final expressions for these forces are found to be

$$\begin{aligned} F_x &\approx 4 \nu_0 k_B T \left(\frac{L}{8A_0 l H}\right)^{1/2} \left(A_0 + \frac{(8A_0 l)^{1/2}}{(LH)^{1/2}} \right. \\ &\times \left.\left(\frac{L^2 - H^2}{LH}\right) \ln \frac{u \tau_-}{a}\right) \frac{L}{\tau_+ u}, \end{aligned} \quad (53)$$

$$\begin{aligned} \Delta F_z &\approx \nu_0 k_B T \left(\frac{A_0 l L}{H}\right)^{3/2} \frac{a}{Ll} - \nu_0 k_B T \left(\frac{LH}{8A_0 l (L^2 - H^2)}\right)^{1/2} \\ &\times \left(A_0 + \frac{(8A_0 l)^{1/2}}{(LH)^{1/2}} \left(\frac{L^2 - H^2}{LH}\right) \ln \frac{u \tau_-}{a}\right) \frac{L}{\tau_+ u}. \end{aligned} \quad (54)$$

A plot of the friction force and the additional normal force versus velocity is shown in Fig. 6.

V. CONCLUSION

In the present article we considered the elastic and friction behavior of liquid-crystalline monolayers, composed of persistent chains grafted on a flat surface. The equilibrium structure of the monolayer is stabilized by orientational in-

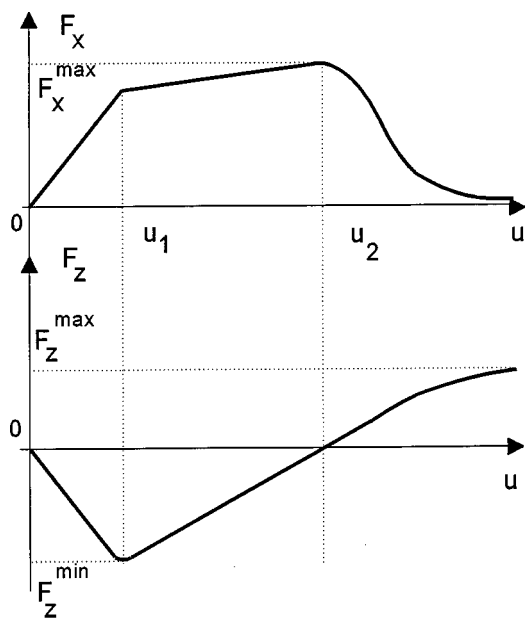


FIG. 6. The plot of the friction force and the additional normal force vs the sliding velocity. $F_x^{\max} \approx \nu_0 k_B T A_0 (L^2/H^2 - 1)^{1/2}$, $F_z^{\min} \approx -\nu_0 k_B T A_0$, $F_z^{\max} \approx \nu_0 k_B T (A_0/L/H)^{3/2} (a/L)^{1/2}$.

teractions, which compensate the loss of entropy due to the stretching of the chains inside the monolayer. Under confinement the monolayer adopts in equilibrium a tilted orientation. The external pressure increases with decreasing the distance H between the surfaces with a power $3/2$, $f_z \propto H^{-3/2}$.

In order to describe the dynamical properties of the confined monolayer we introduced a thin adsorbed layer on the bare surface, so that the adsorption-desorption kinetics for free segments is characterized by a single relaxational time τ , which is connected with an activation barrier. The adsorption-desorption kinetics of the tails of the chains is more complicated and is governed by an additional potential barrier due to the change of the free energy of the chains. Desorption is more difficult than adsorption, and the corresponding desorption time, τ_- , is longer than the adsorption time, τ_+ . Note that both times depend on the chain length and the interaction in the monolayer.

Finally, three regimes of behavior of the friction force can be identified. The first regime is linear and occupies the range of velocities $u < u_1$. Here, the desorption of the chains occurs thermally and the friction force increases linearly with the imposed velocity. In the second regime ($u_1 < u < u_2$) the adsorbed chains attain maximum elongation before they desorb thermally ($u\tau_-$ exceeds the maximum displacement Δx_{\max}) and thus desorb because of the finite extensibility. In this regime there are two contributions to the friction force, namely from the elongating chains and from the breaking chain. The contribution from the elongating chains is independent of the velocity. The second part of the friction force, which is connected with the breaking chains, increases logarithmically with the velocity. The last third regime is characterized by a decrease in the number of adsorbed chains with imposed velocity. This regime takes place when u

$> u_2$. The fraction of adsorbed chains decreases with the velocity as u^{-1} , and thus the friction force also decreases in this regime following the same law.

The effect of the sliding velocity on the normal force was also examined. We found that the additional normal force, which appears under the shear is negative (attractive) in the first two regimes and becomes repulsive in the third regime (the distance between the surfaces, H , is constant). The attraction is connected with an additional normal force, which is induced by the tangential friction force due to nonlinearity. This normal force is proportional to the concentration of the adsorbed chains, and thus becomes small in regime 3. On the contrary the repulsive force arises as the reaction of the desorbed chains, which are compressed and arranged under the adsorbed layer. The fraction of these chains becomes dominant in the third regime and therefore the additional normal force is repulsive in this regime.

Our consideration demonstrates that the tribology of the monolayers is strongly correlated with their nonlinear elasticity. Qualitatively the results are in agreement with the experiments with respect to the dependence of the friction on the imposed velocity.⁹⁻¹³ On the other hand most of the experiments were performed under constant load. Actually, this effect might be considered in the spirit of our model after elimination of the distance H from the equations assuming that the load is constant.

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